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<b>(21) International Application Number:</b> PCT/US98/08232 <b>(22) International Filing Date:</b> 24 April 1998 (24.04.98)  <b>(30) Priority Data:</b> 08/845,709 25 April 1997 (25.04.97) US  <b>(63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application</b> US 08/845,709 (CIP) Filed on 25 April 1997 (25.04.97)  <b>(71)(72) Applicant and Inventor:</b> POLLAK, Richard [US/US]; Suite W, 2120 Jimmy Durante Boulevard, Del Mar, CA 92014 (US).  <b>(74) Agent:</b> REITER, Stephen, E.; Gray Cary Ware & Freidenrich, Suite 1600, 4365 Executive Drive, San Diego, CA 92121 (US).		<b>(81) Designated States:</b> BR, CN, JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> METHOD FOR ENHANCING THE COLOR OF MINERALS USEFUL AS GEMSTONES  <b>(57) Abstract</b>  In accordance with the present invention, there are provided methods for enhancing the color of minerals useful as gemstones. Invention methods are relatively inexpensive to carry out, avoid the use of hazardous materials, and require no specialized equipment.		

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METHOD FOR ENHANCING THE COLOR  
OF MINERALS USEFUL AS GEMSTONES

FIELD OF THE INVENTION

The present invention relates to methods for enhancing the color of gemstones and to novel colored  
5 gemstones produced by invention methods.

BACKGROUND OF THE INVENTION

A variety of materials having the physical and  
10 aesthetic properties desirable for use as gemstones are widely available. However, many of these materials but do not always have an aesthetically pleasing appearance. A variety of procedures have been employed in the art to improve the physical and/or aesthetic properties of  
15 minerals, e.g., electron beam irradiation, Cobalt-60 irradiation, neutron bombardment, exposure to intense heat, and the like.

Each of the above-described prior art methods  
20 suffer from significant drawbacks in terms of cost, safety, efficacy, and the like. For example, Carr, et al., in U.S. Pat. No. 3,950,596, describe methods for coloring corundum crystals by heating them to temperatures of 1600°C or higher while in contact with a powder composed primarily of  
25 alumina, with added metal oxides as colorants. However, even at such high temperatures (where furnace time is expensive) the Carr method requires from 20 to 200 hours. If the temperature were reduced even to 1350°C (well above temperatures employed in the present invention) general  
30 chemical principles would predict that the reaction would take years to run. Furthermore metals such as cobalt, that melt at such high temperatures, cannot be used as colorants.

Other methods are used for coloring non-gemstone alumina. For example, in U.S. Pat. No. 4,732,867, Schnable describes methods for implanting ions such as cobalt in order to make identifying marks in alumina chips. However, as recognized by Schnable, the method is not particularly effective for providing lasting color. Furthermore the colors achieved by ion implantation are not very vivid despite the sophisticated and expensive-to-operate machinery required.

Therefore, it would be desirable to be able to readily impart enhanced and/or modified color to materials useful as gemstones employing readily practiced methods which do not suffer from the drawbacks of prior art methods.

#### BRIEF DESCRIPTION OF THE INVENTION

In accordance with the present invention, methods have been developed for enhancing the color of minerals useful as gemstones, by heating them to moderate temperatures while in contact with powdered cobalt or cobalt oxide (or precursors thereof) and in the absence of alumina. Given the length of time required for prior art methods to take place at much higher temperatures (such as that of Carr, above), under generally recognized chemical principles, one would not expect invention methods to work during the average human lifetime at the moderate temperatures contemplated herein. As shown herein, however, invention methods are useful for enhancing the color of minerals while unexpectedly employing substantially lower temperatures, and for substantially shorter times, than predicted by the prior art. Invention methods are relatively inexpensive to carry out, avoid the use of hazardous materials and require no specialized equipment.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, there are provided methods for enhancing the color of gemstones, 5 said methods comprising:

subjecting a combination of a gemstone and at least one non-alumina treating agent, wherein said treating agent comprises a powdered (i.e., finely divided) form of cobalt metal or cobalt oxide (or precursor thereof) to 10 conditions suitable to enhance the color of said gemstone, without causing a significant level of surface damage to said gemstone.

A wide variety of minerals can be treated 15 according to the present invention. Examples of suitable minerals contemplated for use herein (thereby rendering them useful as gemstones) include topaz, chrysoberyl, sapphire, quartz, garnet, and the like. As used herein, "gemstone" refers to transparent (non-opaque), single 20 crystal minerals useful both as gemstones and/or in optical applications.

A wide variety of metals can be employed in combination with the cobalt metal or cobalt oxide (or 25 precursors thereof) as the major component of treating agent used in the invention process. Examples of suitable metals include transition metals, as well as other metals which can modify the color imparted by the treating agent and/or the mineral being treated.

30

A wide variety of metal oxides can also be employed in combination with the cobalt metal or cobalt oxide (or precursors thereof) as the major component of treating agent used in the invention process, optionally 35 in further combination with a plurality of the metals set forth hereinabove. Examples of suitable metal oxides include transition metal oxides, as well as other metal

oxides which can modify the color imparted by the treating agent and/or the mineral being treated.

Metals and metal oxides contemplated for use in invention methods are preferably employed in a powdered (i.e. finely divided) form in order to maximize contact between the gemstone and the treating agent. As is readily understood by those skilled in the art, a range of particle sizes is suitable for the powdered, or finely divided treating agent. Particles that will pass through the openings of a standard screen of mesh size up to about 400 are contemplated within the present invention. Preferred particles are of a size that will pass through a standard screen of up to about 200 mesh.

15

As used herein, the term "enhance" and any variations thereof, refer to an increase or modification in the color of minerals treated by invention methods, thereby rendering the mineral more valuable as a gemstone. Enhanced colors which can be imparted by the invention process can be varied based on such variables as the particular gemstone being treated, the particular treating agent(s) employed, the conditions to which the gemstones are subjected, and the like. For example, topaz can be modified to have a light blue to dark blue color, or a light green to dark green color, or a light blue-green to dark blue-green color, or a light green-blue to dark green-blue color, depending on the treating agent(s) and treating conditions employed. Similarly, chrysoberyl can be modified to have a light green to a deep blue-green color; sapphire can be modified to have a light blue to a dark blue color (if clear stones are used for treatment) or green, yellow-green or blue-green stones can be produced if the untreated stones are yellow; quartz can be modified to have a light pink to a dark pink color; garnet can be modified to have a green to a blue-green color; and the like.

A wide range of treating conditions can be employed in the practice of the present invention. Typically conditions suitable to enhance the color of a  
5 gemstone, without causing a significant level of surface damage thereto, comprise subjecting the combination of gemstone and at least one powdered (i.e., finely divided) form of cobalt metal or cobalt oxide (or precursors thereof) to a temperature in the range of about 825°C up to  
10 about 1050°C for a time in the range of about 3 up to about 200 hours. Typically such contacting is carried out at ambient pressure.

Generally, longer exposure times and/or higher  
15 exposure temperatures lead to a greater intensity of color being imparted to the mineral being treated, as well as impacting the degree of color saturation achieved by the process. As readily recognized by those of skill in the art, higher treating temperatures are also possible (i.e.,  
20 >1050°C). Such temperatures are likely, however, to cause significant damage to the surface of the mineral being treated, while also providing higher color saturation. The resulting treated gemstone could be polished to remove the surface damage, thereby providing a color-enhanced gemstone  
25 with a satisfactory surface finish.

As will be readily appreciated by those of skill in the art, any method which causes significant surface damage to minerals, thereby requiring additional processing  
30 prior to use of the mineral as a gemstone, will inherently decrease the effective value of minerals so treated. Invention methods are advantageous in that no significant surface damage results to minerals so treated. As will be understood by those skilled in the art, a modest amount of  
35 surface imperfection may occur, however, it can be corrected by minimal additional treatment, such as cleaning

and/or polishing. In a preferred embodiment, minerals treated by invention methods will require no further polishing in order to be suitable as gemstones.

5 As readily recognized by those of skill in the art, the particular temperature ranges and exposure times will not only vary as a function of the intensity and/or level of color saturation desired, in addition, the ability of a given mineral to withstand such exposures without  
10 suffering significant fracturing must also be considered. Thus, for example, quartz would not typically be subjected to conditions as rigorous as topaz.

In a particular aspect of the invention, the  
15 gemstone to be treated can optionally be contacted with a variety of pre-treating agents (e.g., oxygen, reducing agents, and the like) before being subjected to the above-described conditions suitable to enhance the color of a gemstone.

20

Alternatively, or in combination with the above-described gemstone pretreatment, the gemstone can optionally be contacted with a variety of supplemental treating agents (e.g., oxygen, reducing agents, and the  
25 like) while being subjected to the above-described conditions suitable to enhance the color of a gemstone. As will be understood by those of skill in the art, the type of treating agent used will depend on the mineral being treated and the desired end result.

30

An optional additional treatment contemplated for use herein comprises subjecting the treated gemstone to further heating at a temperature in the range of about 825°C up to about 1050°C for an additional length of time in  
35 the range of about 3 up to about 200 hours in the absence of treating agent (i.e., powdered cobalt metal or cobalt



oxide (or its precursors)). Typically such optional additional heat treatment is carried out at ambient pressure. Surprisingly and unexpectedly, such additional heat treatment results in further enhancement of color, even though the gemstone is no longer exposed to the treating agent.

While gemstones can be used in the invention treating process without any special pretreatment, it is presently preferred that gemstones employed in the practice of the invention be cleaned prior to being subjected to said conditions suitable to enhance the color thereof. Suitable cleaning processes are well known to those of skill in the art, and include washing in water, aqueous acid, organic media, and the like.

Gemstones treated according to the present invention can be used directly, or they can be subjected to further treatment and/or washing conditions. It is presently preferred that the treated gemstone be cleaned after being subjected to said conditions suitable to enhance the color of a gemstone. Such cleaning can be accomplished in a variety of ways, e.g., by washing the treated gemstones with aqueous media or with organic solvents (e.g., acetone), by wiping the gemstones with a soft cloth (e.g., a polishing cloth), and the like.

In accordance with another embodiment of the present invention, there are provided color enhanced gemstones having a color enhancing agent diffused into the outer surface thereof. Color enhancing agents contemplated include the treating agents described hereinabove.

In accordance with yet another embodiment of the present invention, there are provided color enhanced gemstones wherein at least the surface of said gemstone has chemically bonded thereto a color enhancing agent. Color

enhancing agents contemplated include the treating agents described hereinabove.

The invention will now be described in greater detail by reference to the following non-limiting examples.

#### Example 1

##### Optional Cleaning Process

10 It is presently preferred that gemstones treated in accordance with the present invention be cleaned as follows. First the stones are treated in gently boiling distilled water containing a small amount of detergent for at least about 12 hours. Once cooled, the stones are then  
15 washed with distilled water until all traces of detergent are removed.

The stones are then soaked at room temperature (or above) in a 1:1 aqueous dilution of concentrated nitric  
20 acid for about two hours, or more. The stones are then rinsed thoroughly with distilled water. The stones are then rinsed with acetone, then rinsed again with distilled water, and dried.

#### Example 2

##### General Treatment Protocol

25 To achieve color enhancement according to the invention, gemstones are placed in a suitable vessel which can withstand the exposure temperatures contemplated for  
30 use (e.g., a flat ceramic sheet, a crucible, and the like) and completely surrounded by the treating agent(s) of choice. The vessel is then placed in a furnace capable of reaching and accurately maintaining temperatures in the range of about 825 up to about 1800°C. The furnace is then  
35 heated to the desired temperature and maintained at that temperature for the desired length of time. Once the

desired time and temperature requirements have been satisfied, the furnace is cooled down and the vessel containing the gemstones is removed therefrom.

5           After the treated gemstones have cooled, they are separated from the treating agent. In many instances, the treated stones need only be wiped clean with a soft cloth or tissue. In some circumstances (e.g., where the stones are subjected to particularly rigorous treating conditions  
10 or where relatively soft stones are treated), it may be desirable to subject the stone to a nitric acid bath to clean the surface of the stone. When such treatment is indicated, concentrated nitric acid solutions or various dilutions thereof can be used.

15

Example 3  
Treatment of Topaz

Topaz can be treated with powdered cobalt metal  
20 or cobalt oxide (or its precursors) to achieve a variety of enhanced colors. For example, treatment at 825°C for about 24 hours results in very light blue stones. Treatment at higher temperature (e.g., 1046°C) for about 24 hours results in much darker blue or blue-green stones. Thus, it  
25 is seen that the final color of the treated stone can be controlled by proper selection of treating conditions.

Once topaz is treated with powdered cobalt metal or cobalt oxide (or its precursors) as described above to  
30 achieve a green-blue or blue-green stone, the color imparted to the stone can be further modified by subjecting the stones to additional furnace heating as described above, but in the absence of treating agent. In this way, the color of the stone can be shifted to blue.

Example 4Treatment of Chrysoberyl

Chrysoberyl is subjected to the same process as described in Example 3. Since the most common color for chrysoberyl is light yellow, the color of the treated stone tends to be yellow-green to blue-green, depending upon the time and temperature of exposure. If a colorless chrysoberyl is used in the process, the enhanced color imparted by treatment with powdered cobalt metal or cobalt oxide (or its precursors) is blue.

Example 5Treatment of Sapphire

15

Sapphire is subjected to the same process as described in Example 3. Care should be taken in selecting the temperature to which the stones are heated, as sapphires tend to develop surface damage when subjected to excessive temperatures. In the event surface damage does occur, the treated stones can be repolished, producing an intensely colored finished product.

The color of the treated stone can vary substantially. For example, a colorless sapphire produces a light blue to dark blue treated stone, depending upon the original color of the sapphire. A yellow sapphire will produce a green, yellow-green to blue-green stone, depending upon the time and temperature of exposure. If a colorless chrysoberyl is used in the process, the enhanced color imparted by treatment with powdered cobalt metal or cobalt oxide (or precursors thereof) is blue.

Example 6Treatment of Quartz

Quartz is subjected to the same process as described in Example 3. Care should be taken in selecting the temperature to which the stones are heated, as quartz tends to develop surface damage when subjected to excessive temperatures. In the event surface damage does occur, the treated stones can be repolished, producing a smooth, colored finished product.

The color of the treated stone can vary substantially, with the invention process typically producing stones which are light to dark pink.

15

Example 7Treatment of Garnet

Garnet is subjected to the same process as described in Example 3. The color of the treated stone can vary substantially, with the invention process typically producing stones which are green to blue-green when light yellow grossular garnet is used.

While the invention has been described in detail with reference to certain preferred embodiments thereof, it will be understood that modifications and variations are within the spirit and scope of that which is described and claimed.

25

That which is claimed is:

1. A method for enhancing the color of gemstones, said method comprising:  
subjecting a combination of a gemstone and at least one non-alumina treating agent, wherein said treating  
5 agent comprises a finely divided form of cobalt or cobalt oxide to conditions suitable to enhance the color of said gemstone, without causing a significant level of surface damage to said gemstone.
2. A method according to claim 1 wherein said gemstone is selected from topaz, chrysoberyl, sapphire, quartz or garnet.
3. A method according to claim 1 wherein said treating agent is cobalt.
4. A method according to claim 1 wherein said treating agent is cobalt oxide.
5. A method according to claim 1 wherein said gemstone is cleaned prior to being subjected to said conditions suitable to enhance the color of said gemstone.
6. A method according to claim 1 wherein said conditions suitable to enhance the color of said gemstone  
comprise subjecting said combination to a temperature in the range of about 825°C up to about 1050°C, for a time in  
5 the range of about 3 up to about 200 hours.
7. A method according to claim 1 further comprising subjecting said gemstone to a temperature in the range of about 825°C up to about 1050°C for a length of time in the range of about 3 up to about 200 hours in the  
5 absence of said treating agent.

8. A method according to claim 1 wherein said gemstone is cleaned after being subjected to said conditions suitable to enhance the color of said gemstone.

9. A color enhanced gemstone prepared by the method of claim 1.

10. A color enhanced gemstone comprising a gemstone having a color enhancing agent diffused into the outer surface thereof.

11. A color enhanced gemstone comprising a gemstone wherein at least the surface thereof has chemically bonded thereto a color enhancing agent.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/08232

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :B05D 1/12, 3/02, 7/00; A44C 17/00

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/180, 190, 191, 217, 383.1; 63/32; 501/86

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3,950,596 A (CARR et al.) 13 April 1976, col. 1, lines 48-55; col. 3, line 30 to col. 4, line 16.	1-2, 4, 9-11
Y	US 4,732,867 A (SCHNABLE) 22 March 1988, col. 1, lines 42-57.	3
Y	US 5,198,265 A (IACOVANGELO et al.) 30 March 1993, col. 4, lines 24-40.	5, 8
Y	US 1,814,219 A (JAEGER et al.) 14 July 1931, pg. 1, lines 90-98.	6
Y	US 4,820,562 A (TANAKA et al.) 11 April 1989, example 2.	7
A	US 4,678,868 A (KRASKA et al.) 7 July 1987.	

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/08232

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3,539,379 A (MAYER) 10 November 1970.	

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/US98/08232

**A. CLASSIFICATION OF SUBJECT MATTER:**

US CL :

427/180, 190, 191, 217, 383.1; 63/32; 501/86

**B. FIELDS SEARCHED**

Electronic data bases consulted (Name of data base and where practicable terms used):

APS, CAPLUS, JAPIO, WPIDS

gem, gemstones, sapphire, topaz, cobalt, cobalt oxide, diffuse, coloring, color, enhance, quartz, garnet, chrysoberyl, powder, particles